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4 **An Overview of California Regional Particulate Air Quality Study Fog Episodes and their**
5 **Effects on Aerosol Formation and Removal**

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23
24 **ABSTRACT**

25
26 Several fog episodes occurred in California's San Joaquin Valley during the winter 2000/01
27 intensive component of the California Regional Particulate Air Quality Study (CRPAQS). Fog
28 measurements at a core study site near the small town of Angiola revealed the fogs to generally
29 be less than 50 m deep, but to contain high liquid water contents (frequently exceeding 200
30 mg/m³) and large droplets. The composition of the fogwater was dominated by ammonium
31 (median concentration = 608 µN), nitrate (304 µN), and organic carbon (6.9 ppmC), with
32 significant contributions also from nitrite (18 µN) and sulfate (56 µN). Principal organic species
33 included formate (median concentration = 32 µN), acetate (31 µN), and formaldehyde (21 µM).
34 A large fraction of dissolved organic carbon appeared to be comprised of large organic
35 molecules, with molecular weights exceeding several hundred Daltons. High concentrations of
36 ammonia resulted in high fog pH values, ranging between 5.8 and 8.0 at the core site. At this
37 high pH aqueous phase oxidation of dissolved sulfur dioxide and reaction of S(IV) with
38 formaldehyde to form hydroxymethanesulfonate are both important processes. The fogs are also
39 effective at scavenging and removal of airborne particulate matter. Deposition velocities for key

solutes in the fog are typically of the order of 1-2 cm/s, much higher than deposition velocities of precursor accumulation mode aerosol particles. Variations were observed in deposition velocities for individual constituents in the order $\text{NO}_2^- > \text{fogwater} > \text{NH}_4^+ > \text{TOC} \sim \text{SO}_4^{2-} > \text{NO}_3^-$. Nitrite, observed to be enriched in large fog drops, had a deposition velocity higher than the average fogwater deposition velocity, due to the increase in drop settling velocity with size. Species enriched in small fog drops (NH_4^+ , TOC, SO_4^{2-} , and NO_3^-) all had deposition velocities smaller than observed for fogwater. Typical boundary layer removal rates for major fog solute species were estimated to be approximately 0.5-1 $\mu\text{g}/\text{m}^3/\text{hour}$, indicating the important role regional fogs can play in reducing airborne pollutant concentrations.

IMPLICATIONS

Measurements of fog composition and deposition of fog borne pollutants indicate that San Joaquin Valley fogs are active processors of airborne pollution. Sedimentation of fog drops during extended fog episodes is an important mechanism for cleansing the atmosphere of fine particles during winter stagnation episodes.

INTRODUCTION

Fogs are comprised of tiny water droplets, typically ranging in size from several micrometers to several tens of micrometers¹. These drops form by water vapor condensation onto aerosol particles known as cloud condensation nuclei (CCN). Water soluble constituents in the CCN determine the initial composition of the fog. Fog drop composition is further influenced by dissolution of soluble gases and aqueous phase chemical reactions. While much has been learned about fog interactions with key inorganic aerosol species (e.g., ammonium sulfate and nitrate), it is only in recent years that investigators have begun examining interactions between fogs and carbonaceous aerosols and volatile organic compounds.

During winter persistent high pressure over the Great Basin of the western United States often creates a strong subsidence inversion over California's Central Valley, with a base typically a few hundred meters off the valley floor and below the surrounding mountain ridges².

71 With the help of the mountains, this strong inversion forms a lid over the air basin, trapping cool,
72 moist air within the valley. Subsiding air results in clear skies, providing excellent conditions for
73 strong radiative cooling at night and, if sufficient moisture is present, formation of dense,
74 widespread radiation fogs.

75
76 Fogs have two important, competing effects on aerosol populations: (1) new aerosol
77 mass formation through gas scavenging and chemical reaction in the droplets leading to non-
78 volatile species (e.g. conversion of SO_2 to sulfate) that remain in the particle phase after droplet
79 evaporation and (2) aerosol particle scavenging followed by deposition through droplet settling
80 and/or impaction. The relative importance of these two processes depends on the environment in
81 which the fog forms: meteorological conditions, number and composition of aerosol particles,
82 gas phase chemical composition, and other factors. The net effect of a fog on atmospheric
83 aerosol concentrations may change during a fog event; oxidation could be more important at the
84 beginning of the fog event when reactant concentrations are higher, while deposition rates may
85 increase over time with the growth of fog droplets³.

86
87 Previous studies of sulfur oxidation in San Joaquin Valley (SJV) fogs have shown that
88 dissolved sulfur dioxide can react rapidly, either being oxidized to sulfate or reacting with
89 carbonyl compounds to form hydroxyalkylsulfonic acids^{4,5}. Variations in fog drop composition
90 with size are known to influence the rates of chemical reactions as well^{6,7}.

91
92 Deposition due to fog drop sedimentation or impaction has been known to be an important
93 removal process for atmospheric pollutants for a long time⁸. Some studies have tried to assess the
94 deposition fluxes by fog in the SJV by modeling³ or by measurements⁹. Relatively few
95 measurements exist, however, regarding atmospheric removal of fog solutes by drop deposition
96 or how drop-size dependent fog composition affects removal rates for individual chemical
97 species.

98
99 While much is now known about the inorganic composition of SJV fogwater, little is known
100 about the scavenging and removal of carbonaceous aerosol by these fogs. Despite measurement
101 of high total organic carbon (TOC) concentrations^{10,11}, the composition of the organic species

making up this TOC is largely unknown in the SJV and elsewhere. Although the net effect of SJV fog episodes is expected to be to reduce atmospheric loadings of carbonaceous aerosol, the magnitude of this removal was unknown prior to the fog study component of the California Regional Particulate Air Quality Study (CRPAQS) reported here.

In order to improve our understanding of the role fogs play in influencing aerosol concentrations in California's Central Valley, Colorado State University made measurements of the chemical and physical properties of fogs at several SJV locations during CRPAQS. These observations form the basis for efforts to better characterize SJV fog composition and interactions between CRPAQS fogs and air pollutants, especially fine particles. Our approach to the study and key study results are summarized here. More detailed information is available in a separate project report¹².

EXPERIMENTAL APPROACH

Colorado State University conducted measurements of fog properties at several SJV sites as part of the CRPAQS¹³ winter intensive. Measurements began in mid-December 2000 and extended through early February 2001. Fog samples were collected during CRPAQS at one core site (Angiola, California) and three satellite sites. The Angiola core site is located in the center of the SJV (35°35'N, 119°32'W, 60m above sea level), surrounded by a large agricultural area. The site was enclosed by a wire mesh fence, where fog collectors and other instruments were set up. Additional automated fog sampling systems were deployed at three satellite sites elsewhere in the SJV: Helm, Bakersfield, and McKittrick. The Helm and McKittick sites were rural, with Helm located north of Angiola and McKittrick in the southern SJV. The Bakersfield satellite site was at an urban location in the city of Bakersfield in the southern SJV. As described below, fog samples were collected at Helm and Bakersfield, but no fog was observed at McKittrick during the period equipment was deployed there.

A Gerber Scientific Particulate Volume Monitor (model PVM-100)¹⁴ was used to provide continuous measurements of liquid water content (LWC) at Angiola. LWC measurements provide a record of fog presence and fog density. When the LWC reaches a threshold value

(usually set at 75 mg/m^3 for a period of 15 minutes), the data acquisition system paged a site operator to come to the site and begin fog collection. PVM calibrations (both of LWC and particle surface area (PSA)) were regularly performed using a manufacturer supplied calibration disk.

A Caltech Active Strand Cloud Collector (CASCC)¹⁵ was used to collect bulk fog samples at Angiola. The CASCC employs a fan to draw air across six rows of $508 \text{ }\mu\text{m}$ Teflon strands. Fog drops are collected based on their inertia. Collected droplets run down the strands, through a Teflon sample trough and Teflon sample tube, and are collected in a polyethylene collection bottle. The lower size cut of this collector as operated during CRPAQS was approximately $3.5 \text{ }\mu\text{m}$ diameter. A Caltech Heated Rod Cloud Collector (CHRCC)¹⁵ was also used in a few fog events when air temperatures fell below freezing. A bulk stainless steel CASCC (ss-CASCC)¹¹ was used to collect fog for analysis of total organic carbon (TOC) and individual organic species by Gas Chromatography / Mass Spectrometry (GC/MS). The design of the ss-CASCC is similar to the CASCC, except the ss-CASCC uses stainless steel walls, stainless steel collection strands, a stainless steel trough and sampling tube, and glass sample bottles. The CASCC, CHRCC and ss-CASCC collectors were used to collect sequential fog samples at time intervals between 1 and 2 hours throughout each fog event. A size-fractionating CASCC (sf-CASCC)¹⁵ was used to collect and analyze drop size-resolved fog samples. The sf-CASCC is similar to the CASCC but has an extra inlet stage (4 rows of eight 12.7 mm diameter Teflon rods) to capture large fog drops. The sf-CASCC was operated during CRPAQS with a 7.5 m/s average sampling velocity, yielding 50% size cuts for the two stages of approximately $21 \text{ }\mu\text{m}$ and $4 \text{ }\mu\text{m}$.

Fog deposition measurements were carried out using two deposition plates. These 0.30 m^2 deposition plates are made of Teflon and have previously been deployed in Davis, California radiation fog⁹. Samples were typically collected at 2 hr intervals to match other cloud composition measurement periods and to provide sufficient sample for composition analysis, including measurement of TOC.

During each fog event collected fog samples were immediately brought to a small field lab for

processing. Samples were weighed to determine collected volume then aliquotted for immediate pH measurement and stabilization of other species for later measurement in our laboratory in Colorado. Fog sample pH was measured on site with an Orion Model 290A or 250A pH meter and a Microelectrodes, Inc. Model MI-710 pH combination electrode, calibrated with pH 4 and 7 buffers.

Sample aliquots were prepared for major ion analysis by pipetting 500 μ l of sample into a polypropylene auto-sampler vial. Inorganic anion (NO_3^- , NO_2^- , SO_4^{2-} , and Cl^-) concentrations were determined using a Dionex DX-500 ion chromatograph equipped with an AG4A-SC guard column, AS4A-SC separation column, a Dionex Anion Self-Regenerating Suppressor (ASRS), and a conductivity detector. Separation was achieved using a 1.8 mM Na_2CO_3 /1.7 mM NaHCO_3 eluent at a flow rate of 2.0 ml/min. Inorganic cation (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) concentrations were determined using a second DX-500 ion chromatograph equipped with Dionex CG-12 and CS-12 guard and separation columns, a Dionex Cation Self Regenerating Suppressor (CSRS), and a conductivity detector. Separation was achieved using a 20 mM methanesulfonic acid eluent at a flow rate of 1.0 ml/min. Both IC systems were calibrated daily using a series of lab-prepared ion standards. Calibration accuracy was monitored by injection of independent, NIST traceable standards.

Formaldehyde was preserved by adding a HCHO preservation solution containing bisulfite (20 mM NaOH, 10 mM CDTA, 3 mM NaHSO_3) to form hydroxymethanesulfonate (HMS). Samples were then analyzed by fluorescence spectrophotometry¹⁶. This method measured the free formaldehyde and any HMS in the solution before preservation. Aliquots were prepared for trace metal analysis by acidification to near pH 1 with trace metal grade nitric acid. Samples were analyzed for Fe and Mn using a Varian Model 640Z Graphite Furnace Atomic Absorption Spectrometer (GFAAS) with Zeeman background correction.

Aliquots for later analysis of organic acids were prepared by addition of a small volume of chloroform, which acts as a biocide. C1-C3 carboxylic acids were analyzed using a Dionex DX500 ion chromatograph (IC) with conductivity detection. The organic acid column in this analysis was a Dionex AS-11 separation column with an AG-11 guard column. Separation was

achieved using a 0.5 mM NaOH eluent at a flow rate of 2.0 ml/min. The IC was calibrated daily using a series of lab-prepared standards.

Sample aliquots for total organic carbon (TOC) analysis were prepared by pipetting 5-20 ml of sample, depending on available sample volume, into a pre-baked glass vial and sealing with a Teflon-lined cap. TOC was measured using a Shimadzu TOC-5000A analyzer. Additional sample was filtered through baked quartz filters (Pall Gelman Pallflex Tissuquartz) to make a distinction between the dissolved phase (dissolved organic carbon, DOC) and the insoluble phase of the fog water.

Several procedures were used to ensure the integrity of each fog measurement, including calibrating instruments, cleaning collectors before each event, taking blanks, and analyzing replicate samples. Minimum detection limits based on collector blanks were well below the measured concentrations for major species reported here. Measurement precision, expressed as relative standard deviations (RSD) and based on replicate fog sample analyses were in the range of 2-8% for TOC, DOC, major inorganic ions (NO_2^- , NO_3^- , SO_4^{2-} , and NH_4^+), organic acids, S(IV), H_2O_2 , and HCHO. RSD for TOC and major ion concentrations in fog deposition samples were in the range of 6-11%.

RESULTS AND DISCUSSION

Several fog episodes were successfully sampled in December, January, and early February. In sum, more than 200 fog samples were collected from the various fog collectors. Figure 1 depicts a timeline of fog liquid water content (LWC) during the study period. The sampled fog events are as follows: Dec 17/18, a good fog event with weather conditions typical of radiation fog, started at 22:15pm and finished at 12:00 noon; Dec 18/19, the fog started at 23:00 pm, then lifted but came back again at 1:20am until 7:30am in the morning; Jan 6th, collected one fog sample from 6:00am to 8:00am using the CHRCC since temperatures were below freezing; Jan 10th, samples were collected from 6:15am to 7:55am; Jan 15th, samples were collected from 23:30 pm to 3:00am; Jan 17th, a freezing fog event lasting from 12:00am to 7:00am; Jan 21st,

samples were collected from 6:00am to 9:00am; Jan 25th, a patchy fog event, occurring intermittently during the period from 3:30am until 8:00am; Jan 31st, a short fog event from 4:00am until 9:30am; Feb 1st, a patchy fog event lasting from 1:00am to 5:20am.

Characteristics of the fogs observed during CRPAQS were somewhat different than we have observed in other SJV radiation fog studies^{10, 17, 18}. During CRPAQS the fog layer was often very shallow, rarely reaching even to the top of the 100 m measurement tower at the core site. In addition, LWC values were high. In our experience, SJV radiation fogs are often rather “thin,” with LWC often less than 100 mg/m³. By contrast, the fogs observed in this study frequently had LWC in excess of several hundred mg/m³. Drop sizes in the CRPAQS fogs were also very large¹², with effective diameters measured by the PVM often in the 20-35 µm range, contributing to rapid settling velocities. At times the drops became so large that the fog began to form what appeared to be drizzle, unusual for such a shallow cloud layer. It is believed that the shallowness of the fog layer probably contributed to direct radiative cooling of fog drops, resulting in strong condensational growth that increased individual drop sizes and overall fog LWC.

Table 1 depicts the concentration ranges (and medians) of bulk fogwater sampled at the Angiola core site during CRPAQS. Figure 2 depicts a typical composition of Angiola bulk fogwater measured during the study. The chemical composition of the fogs was dominated by nitrogen species, with important contributions also from organic compounds and sulfate. Ammonium and nitrate were the most abundant individual compounds; nitrite and sulfate were also found to be present at significant concentrations as were several organic compounds, including formate, acetate, and formaldehyde. Abundant gas phase ammonia absorbed by fog drops helps keep the fog pH relatively high, with pH values typically well above 6. A comparison of measured anion and cation concentrations revealed a charge balance typically within 10%, suggesting that most of the major charged species were probably included in our target analytes.

Comparison of fog composition during CRPAQS at Angiola with compositions measured at Bakersfield and Helm (not shown here) reveals that Angiola and Helm, both rural sites, have generally similar fog compositions. Urban Bakersfield fog contained greater concentrations of

sulfate and nitrite¹². Comparison of Bakersfield fog composition measurements in CRPAQS and other recent SJV fog studies with measurements made in the 1980s¹² reveals a statistically significant decrease in fog concentrations of sulfate and an increase in fog pH. These changes are consistent with intervening declines in SO₂ emissions in the southern SJV, which should translate into less production of sulfate and greater availability of ammonia to raise fog pH.

Results obtained during CRPAQS indicate the important role that SJV fogs play in processing of organic carbon. SJV fogs contain a rich mix of organic compounds, with major constituents including formaldehyde, formate, and acetate. Approximately 25% of the fog organic carbon, on average, is present as undissolved, suspended material in the droplets¹¹. Many larger organic molecules have been previously observed in radiation fogs in Davis, California¹⁹ and were observed here in CRPAQS fogs as well²⁰, indicating active fog processing of particulate organic matter. These observations will be presented in more detail in a future publication. Measurements made using ultrafiltration indicate that as much as half of the fog organic matter may be comprised of high molecular weight compounds, with molecular masses exceeding several hundred Daltons¹¹. Future studies are needed to better characterize this high molecular weight material and determine whether it comes mainly from aerosol scavenging or is produced by aqueous phase reactions of lower molecular weight precursors.

Measurements made with the size-fractionating fog collectors provide insight into the drop size-dependence of various chemical species in CRPAQS fogs. Unlike previous SJV fog studies^{17,18} in a more urban area (Davis, California), the pH values of large and small CRPAQS fog droplets didn't show a large difference. For inorganic species, significant concentration differences were seen between large and small drop fractions. Chloride, ammonium, sulfate, nitrate, potassium, manganese, calcium were all enriched in smaller drops; total Fe and Mn showed no preference of enrichment; nitrite was enriched in larger drops. These trends were reinforced by observations made with the CSU 5-stage cloud collector^{21,22} also deployed at Angiola during CRPAQS. Figure 3 illustrates the size-dependent composition observed for sulfate and nitrite, examples of species observed to be enriched in small and large drops, respectively. The size dependence of many of the species observed here is consistent with patterns observed previously in SJV fogs^{10, 17,18}.

For organic species, TOC was observed to be strongly enriched in small drops¹¹. Formic acid showed a weak trend of enrichment in small drops. Acetic acid shows a trend similar to formic acid. Analysis of the size-dependence of these low molecular weight carboxylic acids has been presented elsewhere²³.

Observations of the deposition fluxes of fog water and measured solute species were analyzed, in conjunction with measured airborne fogwater solute concentrations and LWC, to obtain deposition velocities. The approach taken here is similar to analyses we have conducted previously for Davis, California, radiation fogs^{9,18}. As observed in Davis, deposition velocities varied significantly between solutes. Figure 4 presents the average (along with the range) deposition velocities determined for fogwater and for several key fog solutes. One readily notes the relatively high deposition velocities, typically on the order of 1-2 cm/s, much higher than expected for ammonium nitrate, ammonium sulfate, or organic carbon contained in accumulation mode aerosol particles. Such high deposition velocities lead to rapid removal of air pollutants during extended fog episodes.

The average deposition velocity was lowest for nitrate and highest for nitrite. Overall the order of average deposition velocities was $\text{NO}_2^- > \text{water} > \text{NH}_4^+ > \text{TOC} \sim \text{SO}_4^{2-} > \text{NO}_3^-$. The observed trends in solute deposition velocities reflect the non-uniform distribution of fog solutes across the fog drop size spectrum. Solute species that tend to be enriched in large drops (e.g., NO_2^-) experience high deposition velocities because of the strong increase in drop sedimentation rate with drop size. Nitrite, in fact, was observed to have a deposition velocity that exceeded the average deposition velocity of fogwater, due to its enrichment in faster settling, large fog drops. Species that were observed to be enriched in small fog drops (NH_4^+ , TOC, SO_4^{2-} , and NO_3^-) all had deposition velocities less than the average fogwater deposition velocity. One can even relate the relative deposition velocities of the various species (and water) to their degree of enrichment in small fog drops. Figure 5 illustrates this for three sample fog periods, revealing that the more strongly a species is enriched in small fog drops the lower its deposition velocity falls. Significant differences in deposition velocities between time periods often arise, as seen in Fig. 5, due to changes in fog microphysical properties.

Table 2 lists computed species mass removals for each CRPAQS fog event. Longer fog events tend to produce greater mass removal amounts. Taking into account fog duration and measured fluxes, a typical fog episode in CRPAQS removed approximately 50 $\mu\text{g}/\text{m}^2/\text{hr}$ of sulfate, 110 $\mu\text{g}/\text{m}^2/\text{hr}$ of nitrate, 100 $\mu\text{g}/\text{m}^2/\text{hr}$ of ammonium, and 70 $\mu\text{gC}/\text{m}^2/\text{hr}$ as TOC.

In CRPAQS the typical fog layer was less than 50m high. If we consider a conservative case where the measured fluxes of material are removed from a column 100m deep, we can estimate the effects of CRPAQS fog episodes on boundary layer pollutant concentrations. For a typical CRPAQS fog episode, we estimate ambient concentration reductions of approximately 0.5 $\mu\text{g}/\text{m}^3/\text{hr}$ of sulfate, 1.1 $\mu\text{g}/\text{m}^3/\text{hr}$ of nitrate, 1.0 $\mu\text{g}/\text{m}^3/\text{hr}$ of ammonium and 0.7 $\mu\text{gC}/\text{m}^3/\text{hr}$ in the form of TOC. These numbers are quite significant and indicate the effective role these fogs play as atmospheric cleansers. It is important to keep in mind, however, that some of the deposited material may be volatile (but water soluble) and subject to partial emission back into the atmosphere if the wetted ground dries following fog evaporation.

Removal of scavenged particulate species can of course be offset by aqueous phase conversion of volatile precursors to non-volatile products. The high pH droplets present in CRPAQS fogs make them effective atmospheric reactors for dissolved sulfur dioxide. Both oxidation to sulfate and reaction with dissolved formaldehyde to produce hydroxymethanesulfonic acid (HMS) are known to be important pathways for new particle mass production in SJV fogs^{3,4,5,7,24}. Numerical simulations using an updated version of a single drop fog chemistry model⁷ reveal the importance of both sulfate production and formation of HMS in fogs during CRPAQS. Frequent observations of HMS in individual SJV particles during CRPAQS (Prather, personal communication) and during previous studies²⁵ are consistent with the importance of this reaction pathway. Comparisons of fine particle organic carbon concentrations before and after CRPAQS fog episodes also suggest that aqueous phase reactions of dissolved VOCs may be important in producing new, secondary organic aerosol matter as suggested elsewhere²⁶. More work is needed to examine this hypothesis in future investigations.

The Carnegie Mellon University fog model^{3,6,27}, a drop size-resolved fog model with explicit fog microphysics, was used to simulate a CRPAQS fog episode and was able to predict the liquid water evolution, bulk aqueous-phase concentration measurements, drop size-resolved trends, and deposition fluxes for a number of species in close agreement with observed values²⁸. During the early stages of the fog, the behavior of species originating partially in the gas phase (NO_3^- , SO_4^{2-}) was heavily influenced by dissolution into the droplets and rapid aqueous phase reactions. Following these initial peaks in aqueous phase concentrations, deposition began to dominate, and the species were gradually depleted from the fog layer. These findings are similar to earlier model simulations of SJV fogs³ where the net effect of the fogs on inorganic nitrogen species was removal while production and removal of sulfate were more closely balanced.

CONCLUSIONS

Several San Joaquin Valley fog episodes were characterized during CRPAQS. Most of the fog episodes were relatively shallow and featured very large droplets. The chemical composition of the fogs was dominated by nitrogen species, with important contributions also from organic compounds and sulfate. Ammonium and nitrate were the most abundant individual compounds; nitrite and sulfate were also found to be present at significant concentrations as were several organic compounds, including formate, acetate, and formaldehyde. Abundant gas phase ammonia absorbed by fog drops helps keep the fog pH relatively high, with pH values typically well above 6. The high pH droplets present in CRPAQS fogs make them effective atmospheric reactors for dissolved sulfur dioxide. Both oxidation to sulfate and reaction with dissolved formaldehyde to produce hydroxymethanesulfonic acid (HMS) are important reaction pathways.

Previous studies have documented the important role SJV fogs play in cleansing the atmosphere via particle scavenging followed by drop deposition. The importance of this mechanism was again observed during CRPAQS, with fog deposition fluxes capable of reducing boundary layer atmospheric concentrations of major species (e.g., nitrate, ammonium, and organic carbon) at a rate on the order of $0.5\text{--}1\ \mu\text{g}/\text{m}^3\ \text{hr}$. The fogs are also effective at scavenging and removing sulfate, but this removal is offset by production of new, non-volatile

sulfur compounds via aqueous phase chemistry. Preferential enrichment of major ion species in small fog drops reduces most species' deposition velocities below the deposition velocity for fog water. Nitrite, which was often enriched in large fog drops, exhibited deposition velocities higher than fog water. Accounting for drop size-dependent species concentrations is essential to accurately modeling rates of pollutant deposition in SJV fogs.

While the CRPAQS fog study has increased our understanding of the importance of fog processing of both inorganic and organic aerosol species, a significant need remains to continue studies of this type. In particular, our understanding of the production and removal of fine particle organic carbon remains in its infancy. Much more work is needed to elucidate the relative efficiencies with which fogs scavenge and deposit carbonaceous particles from different source types and to determine the extent of secondary organic aerosol formation occurring via aqueous phase reaction pathways that convert soluble VOCs to nonvolatile products that are released as aerosol particles when a fog evaporates.

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Table 1. Summary of bulk fog sample composition

Species	Number of samples	Concentration Range	Median
pH (pH units)	36	5.85-8.04	6.73
Cl ⁻ (μN)	36	10.5-39.8	16.3
NO ₃ ⁻ (μN)	36	78.1-1872.1	303.5
NO ₂ ⁻ (μN)	36	4.7-131.9	17.7
SO ₄ ²⁻ (μN)	36	12.9-329.5	56.5
Formate (μN)	22	14.9-120.7	31.6
Acetate (μN)	22	5.0-197.2	31.4
Propionate (μN)	22	ND ^a -10.4	1.7
Pyruvate (μN)	22	ND-0.7	0.7
Oxalate (μN)	22	3.2-24.9	7.2
Na ⁺ (μN)	36	0.13-22.5	5.8
K ⁺ (μN)	36	1.9-18.6	4.3
NH ₄ ⁺ (μN)	36	193.2-2203.7	608.3
Mg ²⁺ (μN)	36	4.2-24.8	5.3
Ca ²⁺ (μN)	36	5.6-101.5	10.7
HCHO (μM)	36	2.6-49.3	21
Fe (μg l ⁻¹)	24	16.9-341.9	77.5
Mn (μg l ⁻¹)	24	0.9-16.5	4.1
TOC (ppmC)	22	2.3-41.9	6.9

ND^a Not detected- the response was below the detection limit for this species.

Table 2. Total mass removal of species by fog episodes during CRPAQS.

Fog Episode Start Date	Sample Time (hour)	NO ₃ ⁻ (µg/m ²)	SO ₄ ²⁻ (µg/m ²)	NH ₄ ⁺ (µg/m ²)	TOC (µgC/m ²)
12/18/2000	9.0	2246	1223	2627	952
12/19/2000	2.3	127	50	203	72
1/15/2001	2.0	51	22	71	75
1/17/2001	7.8	393	174	526	309
1/21/2001	3.0	774	173	448	312
1/25/2001	2.5	37	26	70	66
1/31/2001	3.8	592	251	463	452
2/1/2001	1.7	96	71	101	113

FIGURE CAPTIONS

Figure 1. Timeline of fog LWC during the CRPAQS study winter intensive in 2000/01.

Figure 2. Typical major species composition (by mass) for Angiola fog during winter 2000/2001.

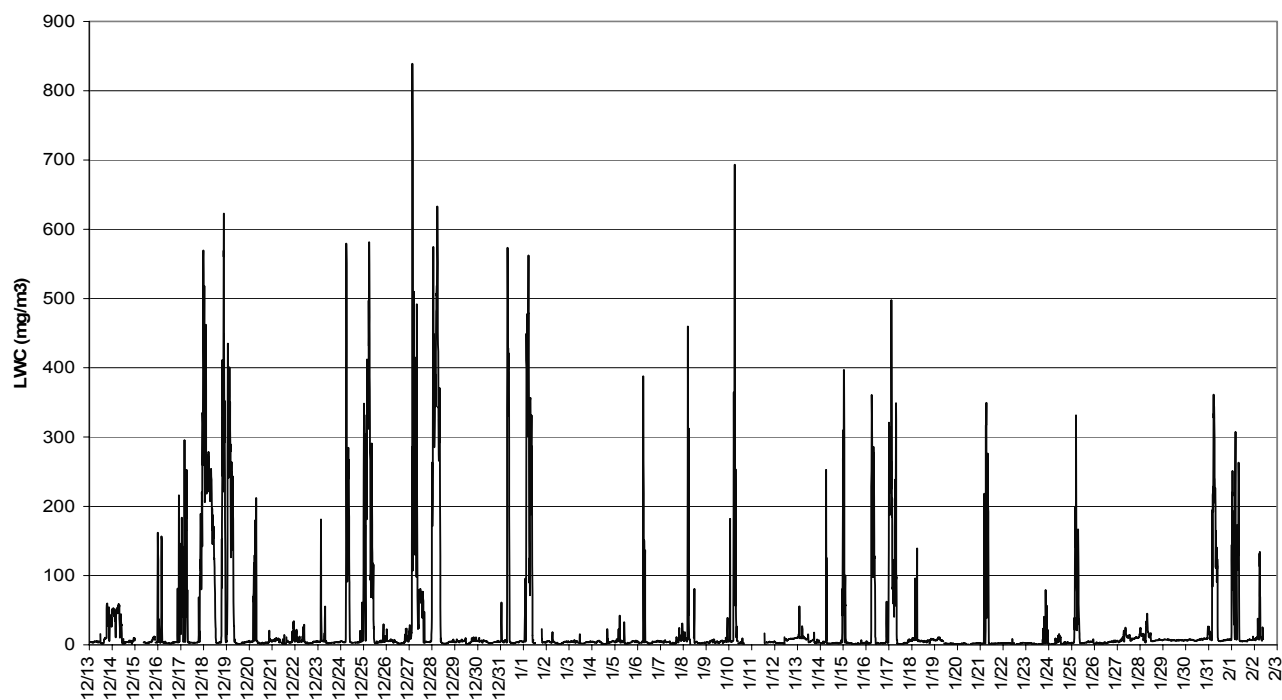
Figure 3. Drop size-dependent concentrations of sulfate and nitrite observed in CRPAQS fogs. Samples were collected with the sf-CASCC. Nominal size ranges for the small and large drop size fractions are 4-21 µm and > 21 µm diameter, respectively.

Figure 4. Average deposition velocities (+/- range) observed for fog water and several key solute species in CRPAQS fogs. Deposition velocities are arranged from lowest to highest for comparison purposes.

Figure 5. Deposition velocity vs. small/large drop concentration ratio for three CRPAQS fog samples obtained using the sf-CASCC. Points are plotted from left to right in each series for NO₂⁻, NH₄⁺, SO₄²⁻ and NO₃⁻, respectively. The more strongly a species is enriched in small fog drops the lower its deposition velocity tends to be.

Figure 1

LWC observed in Angiola during CRPAQS



CRPAQS typical fog mass composition

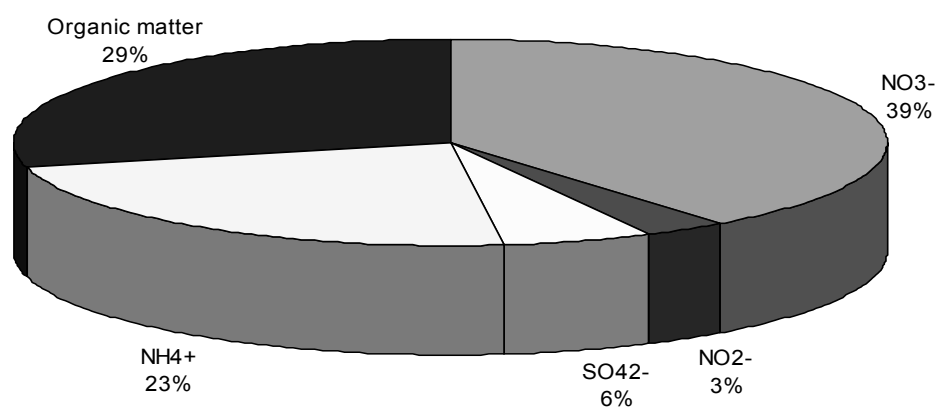


Figure 2

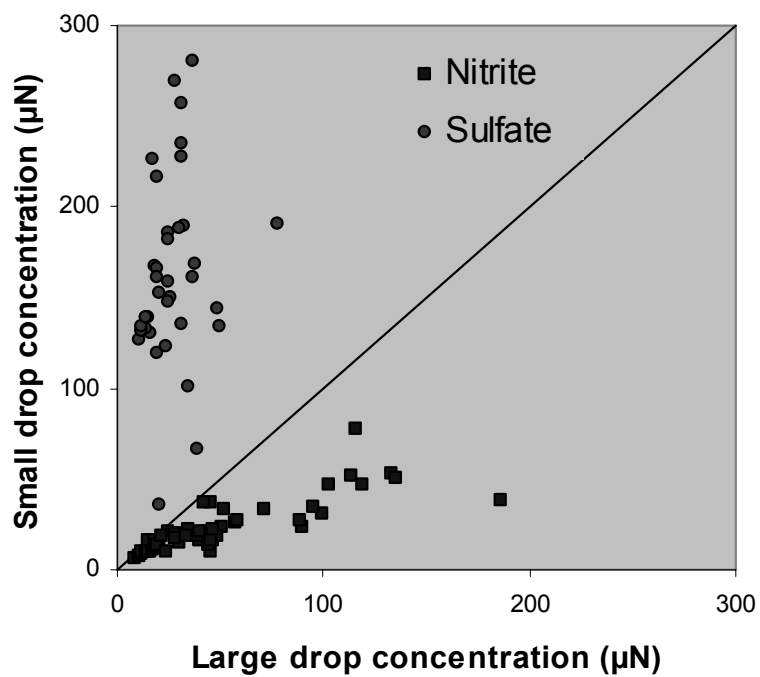


Figure 3

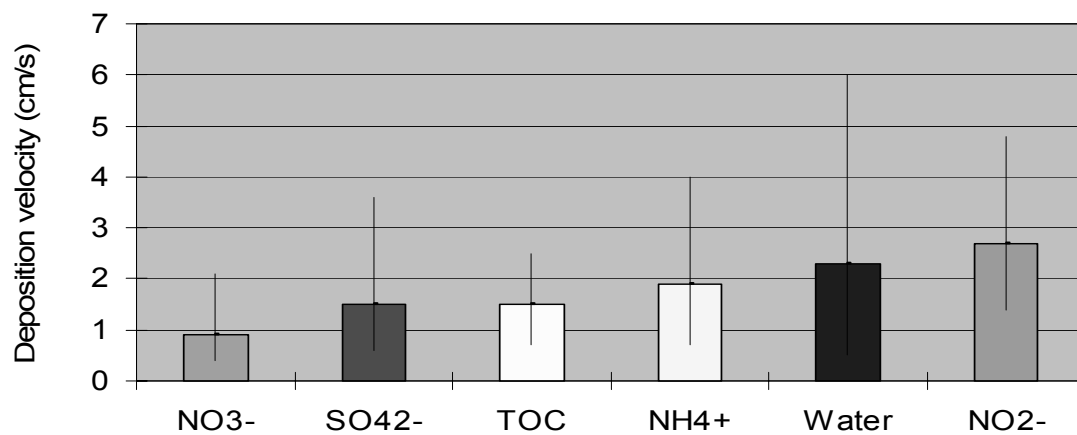


Figure 4

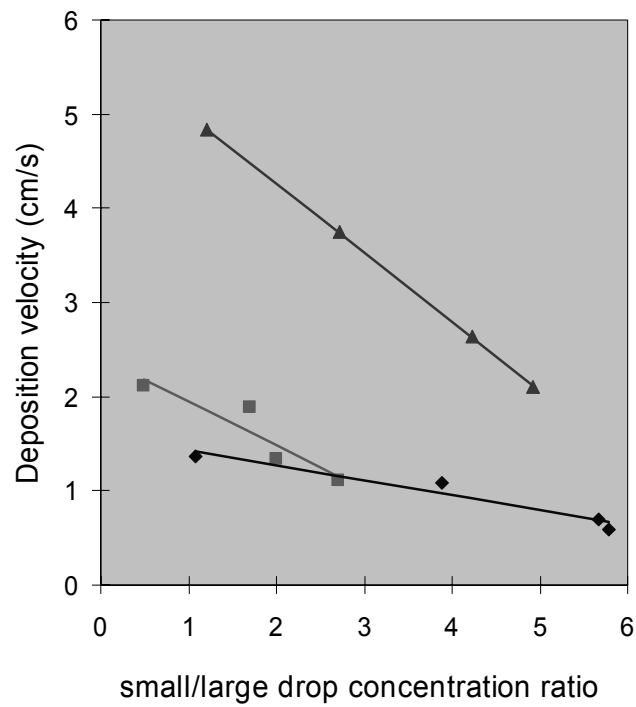


Figure 5